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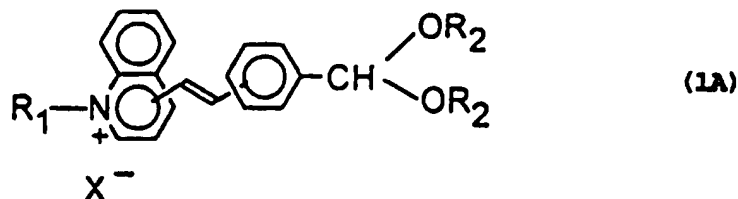
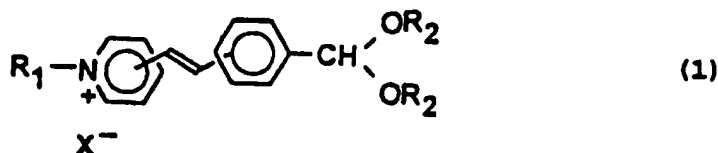
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07D 213/46, 215/14, G08F 8/30, 8/32, G03C 1/71		A1	(11) International Publication Number: WO 96/29312
			(43) International Publication Date: 26 September 1996 (26.09.96)
(21) International Application Number: PCT/KR96/00035		(81) Designated States: CN, JP, MX, US, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 20 March 1996 (20.03.96)			
(30) Priority Data: 1995/5821 20 March 1995 (20.03.95) KR 1995/5822 20 March 1995 (20.03.95) KR		Published With international search report.	
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(54) Title: STILBAZOLIUM SALT, AND PREPARATION AND USE THEREOF

(57) Abstract

The present invention relates to a stilbazolium salt represented by formula (1) or (1A), wherein R₁, R₂ and X⁻ are as defined in claim 1; a process for preparing thereof by using terephthalaldehydemonodi-alkylacetal; and use of thus prepared stilbazolium salt for preparation of a photosensitive resin.



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STILBAZOLIUM SALT, AND PREPARATION AND USE THEREOF**TECHNICAL FIELD**

5 The present invention relates to novel stilbazolium salt, and preparation and use thereof. More specifically, the present invention relates to novel stilbazolium salt prepared by using terephthalaldehydemonodialkylacetal, processes for preparation thereof, and use of thus prepared stilbazolium salt for preparation of a photosensitive resin.

10 Stilbazolium salt ("SbQ salt") forms a photosensitive resin of high sensitivity ("PVA-SbQ type resin") when it is combined with polyvinyl alcohol ("PVA"). By properly mixing a fluorescence and other additives thereto, a slurry, which is used for preparation of color Braun tube as a raw material, is
15 formed.

BACKGROUND ART

 The PVA-ADC (ammonium dichromate) type photosensitive resin or PVA-Diazo type photosensitive resin has been commonly
20 used as a photosensitive resin for fluorescent slurry of color Braun tube. However, the PVA-ADC type or PVA-Diazo type resin has been recently substituted with the PVA-SbQ type resin because it exhibits from several to several dozens of more folds of activities as compared to the conventional PVA-ADC
25 type or PVA-diazo type photosensitive resin, and thus the former two types are presently considered as highly valuable for the purposes of fixation of enzyme, screen printing, preparation of color picture tube, color filter or the like. In addition, a photosensitive liquid using the PVA-SbQ type
30 resin has a great advantage in that it causes very little environmental pollution unlike the conventional photosensitive resin. The conventional PVA-ADC type photosensitive resin contains chromium, a type of heavy metal, and PVA-diazo type photosensitive resin contains a large amount of toxic diazo
35 compound in order to increase sensitivity, so that both resins are serious environmental hazards. Thus, there has been an urgent need to find a substitute for these resins, and the PVA-

SbQ type resin is presently being used as a substitute for the PVA-ADC or PVA-diazo type resin. On the other hand, the problem with the PVA-SbQ type resin is that the process of preparing SbQ salt, used as a raw material of the resin, is complicated and inefficient. Therefore, development of a process for efficient preparation of SbQ salt is required in the art.

Two processes for the synthesis of the aforementioned SbQ salt are suggested in Japanese Patent Laid Open No. 55-24126. In these processes, however, terephthalaldehyde ("TA"), as a reactant, is used in 2 - 3 or more folds in order to minimize the dimeric byproduct produced by side-reactions. Besides, a large amount of TA is consumed because the unreacted TA is not recovered after the reaction, but recovering the unreacted TA requires additional costs.

These two processes are described in detail below.

The first process comprises reacting a compound of picoline type or methylquinoline type with terephthalaldehyde; purifying the product thus obtained; and reacting the product with an alkylating agent to synthesize SbQ salt. However, the process has problems in that 1) an excess amount of TA is used in order to avoid dimeric byproduct, 2) the material used in the purifying process is very toxic, and 3) a complicated process comprising 7 steps (i.e., (a) removing the unreacted TA by using aqueous hydrochloric acid, (b) removing the unreacted TA by using benzene, (c) neutralizing with aqueous sodium hydroxide, (d) drying SbQ and dimeric byproducts, (e) removing the dimeric-byproducts by using ethyl acetate, (f) removing the ethyl acetate and drying SbQ, and (g) synthesizing SbQ salt by using dimethyl sulfate) are required.

The second process comprises reacting a compound of picoline type or methylquinoline type with an alkylating agent, and adding TA to the reaction mixture to prepare SbQ salt. In this process, multi-step purifying process has been somewhat simplified, but the problem of using an excessive amount of TA still remains. The process for purifying SbQ salt according to the second process comprises the steps of (a) removing the

dimeric byproduct from the reaction mixture, (b) treating the reaction mixture with a mixed solvent of ethanol and acetone, and (c) filtering and drying SbQ salt. Although the complicated purifying processes have been simplified somewhat in this three-step process, a method of removing the dimeric byproducts has not been described.

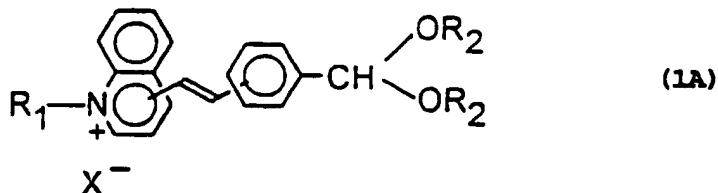
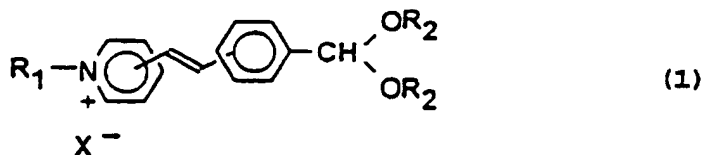
DISCLOSURE OF INVENTION

After the present inventors have researched and experimented to develop various types of SbQ type compounds in order to solve the problems mentioned above, and as a result, the inventors have discovered that a novel photosensitive group can be manufactured in a large amount by using a material of which one of the two aldehyde groups had been protected by acetal group, i.e., terephthalaldehydemonodialkyl acetal ("TDA"), so as to prevent the consumption of excessive TA and to simplify the preparation process.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described in more detail below.

The present invention provides a stilbazolium salt ("SbQ-A salt") as a photoreactive compound which is represented by the following formula (1) or (1A):



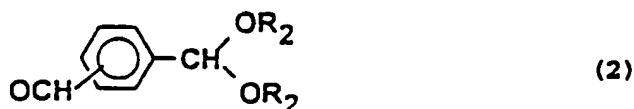
wherein, R_1 and R_2 , being identical to or different from each other, independently represents hydrogen atom, alkyl group, aryl group, allyl group, aralkyl group or allylalkyl group, wherein hydroxyl group, amide group, carboxylic group, ether bond, double bond, or the like may be included in each group; and X^- represents halogen ion, sulfate ion, phosphate ion, methosulfate ion, methanesulfonate ion or p-toluenesulfonate ion.

The present invention provides two processes for preparing the aforementioned novel SbQ-A salt. The first process of the present invention comprises the steps of reacting a compound of picoline type or methylquinoline type with TDA, and purifying the reaction product to obtain pale yellow crystals, and dispersing the crystals thus obtained in water, and adding an alkylating agent of the following formula (3) thereto to obtain the stilbazolium salt.

The second process of the present invention comprises the steps of reacting a compound of picoline type or methylquinoline type with an alkylating agent of the following formula (3) to form a picolinium salt or methylquinolinium salt, and adding TDA to the solution thus obtained, and heating under reflux to obtain clear yellow SbQ-A salt.

Compounds of picoline type or methylquinoline type include α , β or γ -picoline or 2-, 3-, 4-, 6-, 7- or 8-methylquinoline.

The aforementioned TDA used in the preparation of SbQ-A salt of the present invention is a compound represented by the following formula (2):



wherein, R_2 represents hydrogen atom, alkyl group, aryl group or allyl group, and each R_2 may be of the same group and each

of the three groups may include hydroxyl group, amide group, carboxylic group, ether bond, double bond, or the like. Among these, a representative example is terephthalaldehydemonodiethylacetal.

5 The alkylating agent used in the formation of SbQ-A salt of the present invention is a compound represented by the following formula (3):



10

wherein, R_1 represents hydrogen atom, alkyl group, aryl group, allyl group, aralkyl group or allylalkyl group, wherein hydroxyl group, amide group, carboxylic group, ether bond, double bond, or the like may be included in each group; and X represents halogen atom, sulfate group, phosphate group, metho-

15 sulfate group, methanesulfonate group or p-toluenesulfonate group.

Among these, representative examples are dimethyl sulfate, p-toluenesulfonate, and so on.

20

The solvent used in the synthesis of SbQ-A salt according to the first process described above is not restricted, and a mixed solvent of acetic anhydride and acetic acid should preferably be used. The temperature of the reaction can be varied depending on the solvent used. The temperature should

25 be between room temperature and 180°C, and the reaction time should be between 1 hour to 24 hours, preferably 7 to 11 hours.

25

The solvent used in the synthesis of SbQ-A salt according to the second process described above include polar solvents such as methyl alcohol, ethyl alcohol, or the like. Usable catalysts include acids and bases. In particular, sodium

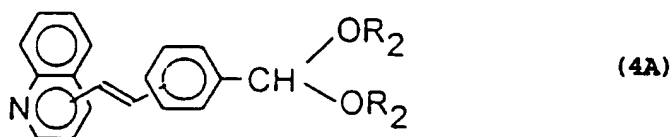
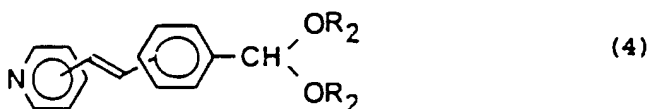
30 hydroxide, sodium ethoxide, sodium acetate or amine compounds may be used as a base catalyst. Use of weak bases rather than strong bases, is more efficient and preferable. A representative example is piperidine.

30

35

The two processes according to the present invention are explained in more detail below by means describing preferred embodiments.

In the first process of the present invention, a compound of picoline type or methylquinoline type and TDA are heated under reflux in a mixed solvent of acetic anhydride and acetic acid for 1 to 24 hours, a large amount of water is added thereto, and the resultant solution is neutralized with dilute alkaline solution to give pale yellow precipitate. The precipitate is filtered, and washed with methyl alcohol, isopropyl alcohol, or the like, and filtered and dried to obtain crystals of compound represented by following formula (4) or (4A):

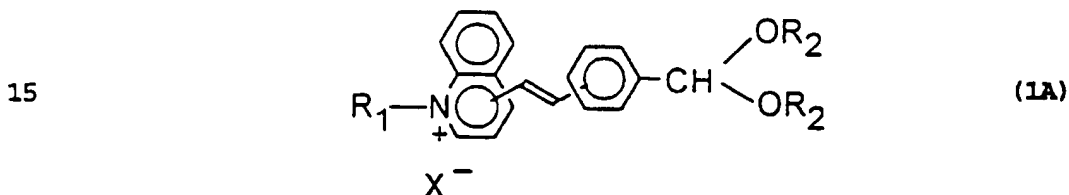
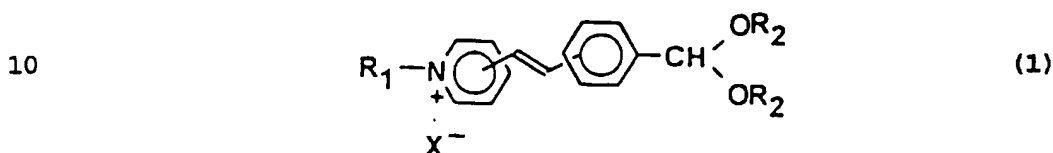


wherein, R_2 is defined as above.

Of course, a compound of which the acetal site of formula (4) or (4A) has been converted to aldehyde may be detected in a small amount if such acidic solvent was used. When the compound is reacted with the alkylating agent, SbQ salt, not SbQ-A salt is formed. The formation of the compound having the converted aldehyde group is caused by water produced by a condensation reaction between picoline or methylquinoline compound and TDA, and acidic solvent. Thus, in order to completely delete the possibility of formation of the compound having the converted aldehyde group, a base catalyst is used instead of acidic catalyst since the acetal site of the formula (4) or (4A) may stably co-exist with basic compound though it is fragile to acidic compound.

The crystals thus obtained is dispersed in water, and an

alkylating agent such as dimethyl sulfate is added to the dispersion to form SbQ-A salt. Upon completion of the salt formation, water is immediately removed by using a rotary evaporator, and the residue is washed with acetone and dried to give clear yellow SbQ-A salt of the following formula (1) or (1A):



wherein, R_1 , R_2 and X^- are as defined above.

20 The salt thus obtained is completely soluble in water. A photosensitive resin is prepared by adding acid catalyst such as phosphoric acid to the aqueous solution of the salt and then reacting it with aqueous PVA solution.

25 In the second process of the present invention, a compound of picoline or methylquinoline type is dissolved in a methyl alcohol solvent and the solution is cooled at low temperature. An alkylating agent such as dimethyl sulfate is slowly added thereto to form a picolinium salt or methylquinolinium salt. After stirring the reaction mixture for about 1 hour, TDA is added, and the mixture is heated under reflux for 30 minutes to about 24 hours. Methyl alcohol solvent is removed therefrom by using a rotary evaporator, and the residue is washed with acetone to form a deposit of clear yellow SbQ-A salt crystals. The crystals are filtered and dried to give SbQ-salt having a structural formula or (1) or (1A) as described above.

The second process of the present invention is different

from the first process in that (a) it comprises different reaction orders of the reactants used for preparing SbQ-A salt from those of the first process, and (b) the aldehyde formation of the acetal site caused by the use of acid catalyst in the first process does not occur. Thus, the second process for preparing SbQ-A salt according to the present invention is more efficient than the first process.

The processes according to the present invention have advantages described below when compared to the conventional processes.

In the conventional processes, substantial dimeric byproducts are produced owing to the use of TA, which is reacted with a compound such as α -, β -, γ -picoline or methylquinoline, or α -, β -, γ -picolinium salt, or methylquinolinium salt, resulting in large consumption of TA and the huge cost associated with it. The present invention solves this problem by using a material (TDA) of which one aldehyde group of TA have been protected by an acetal group, instead of TA. For the purifying process, a step for removing the unreacted TA is urgently needed in the conventional process owing to the use of large amounts of TA. A process for removing the dimeric byproducts also is essential because the production thereof cannot be completely avoided even if a large amount of TA is used.

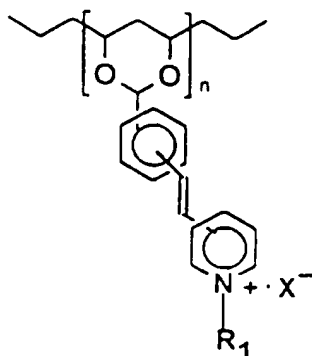
In contrast, the process for removing the unreacted TA as well as that for removing the dimeric byproducts is unnecessary in the processes of the present invention, by using TDA instead of TA, whereby the overall process is shortened. This is because the production of dimeric byproducts is prevented by an effect of acetal group of TDA which protects aldehyde group from dimer formation, and TDA itself exists as a liquid phase at room temperature so that the purifying steps after the SbQ-A salt formation may become easy.

The SbQ-A salt of the present invention thus obtained, as combined with completely or partially saponified polyvinyl acetate, can be used for the preparation of photosensitive resin having a structure of the following formula (5) or (5A)

which can perform a cross-linking reaction upon exposure to light. Such a use also is included within the scope of the present invention.

5

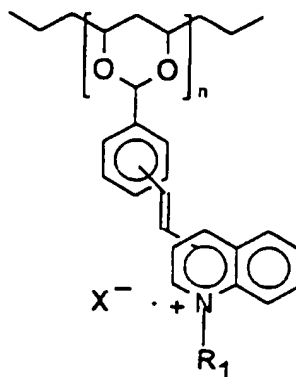
10



(5)

15

20



(5A)

25

wherein, R_1 and X^- are defined as above.

The polymerization degree of the polyvinyl alcohol (completely or partially saponified polyvinyl acetate) used for preparing the photosensitive resin by the use of SbQ-A salt according to the process described above, is preferably 300 - 3000, and saponification rate thereof is preferably 75% or more.

The reaction of SbQ-A salt with PVA in the presence of acid catalyst must be performed in a darkroom because the reaction mixture itself exhibits high photosensitivity as the reaction proceeds. The reaction temperature is preferably 0 to 100°C, and the reaction time of 1 to 50 hours is sufficient.

35

Since the finished reaction mixture has high photosensitivity, the photosensitivity may be tested with the reaction mixture, or it may be tested after re-precipitating in acetone, methanol, dioxane or the like, extracting with methanol by the use of Soxhlet device and drying. The photosensitive resin thus obtained, even if the incorporated ratio of photosensitive group is only 1 mol%, exhibits from several to several dozen-folds of activities, as compared to the conventional PVA-ADC type or PVA-diazo type resin. Maximum absorption range appears around 340 nm.

When the overall reaction process is examined, PVA-SbQ can be prepared by using the same 2 reactors of the conventional processes, though TDA has an acetal group at an end unlike TA. Both processes for preparing SbQ-A need only one reactor, and SbQ-A salt may be used, together with an aqueous PVA solution separately prepared, for the preparation of PVA-SbQ photosensitive liquid in one reactor. It is because an aldehyde formation of the acetal occurs by an acid catalyst during the reaction of SbQ-A salt with PVA, even if one side of TDA is comprised of acetal, and the aldehyde can be re-acetalized by reacting with two hydroxyl groups in PVA.

The acid catalyst has two roles of altering the acetal in SbQ-A salt to aldehyde and of re-acetalizing the altered aldehyde, so that the consumption of the acid catalyst may be reduced. More specifically, one reactor is needed to prepare SbQ-A in the first process, and another reactor is needed to prepare SbQ-A salt by the reaction of SbQ-A with an alkylating agent. An aqueous solution of PVA which have been prepared separately is added to the aqueous solution containing SbQ-A salt, and the mixture is reacted in a darkroom to obtain an aqueous PVA-SbQ solution. Alternatively, the same is applied if the acetal site of SbQ-A salt dissolved in water is altered to aldehyde by heating under reflux and then the product is reacted with the aqueous PVA solution. Further, one reactor is needed to prepare SbQ-A salt in the second process, and another reactor is needed to dissolve SbQ-A salt in water. An aqueous solution of PVA which have been prepared separately is added to

the aqueous solution, and an acid catalyst, and the mixture is reacted to obtain a photosensitive resin. Of course, it is possible to directly add the SbQ-A salt and the acid catalyst to the aqueous solution of PVA and carry out the reaction.

5 Thus, the preparation of SbQ-A salt is more efficient than that of SbQ salt. Since the acetal group of SbQ-A salt can be readily converted to an aldehyde group in acidic solution and then can be re-acetalized by reacting with the hydroxy group of PVA, the problems associated with the
10 conventional processes do not exist in the reaction with PVA.

From these viewpoints, the process of the present invention is able to prepare PVA-SbQ more efficiently than by the conventional processes, allowing a large scale manufacture of PVA-SbQ resin.

15

BEST MODE FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention will be described in more detail, referring to the Examples and Comparative Examples. However, it should be noted that the present
20 invention is not restricted to these Examples.

Example 1

4-Picoline (33.99 g) and terephthalaldehydemo(d-diethylacetal) (76.02 g) were added to a mixed solvent of acetic acid (28.60 g) and acetic anhydride (61.25 g), and the mixture
25 was heated under reflux for 11 hours. The hot reaction mixture was poured into about three-folds of water, and the resultant mixture was then neutralized to pH=7 by using 10% by weight of sodium hydroxide aqueous solution. As sodium hydroxide aqueous
30 solution were being added, the reaction product was precipitated as a slurry, which was then filtered. The product obtained by filtration was dispersed in isopropyl alcohol. The dispersion was stirred for 1 hour, so that the unreacted materials may be dissolved in isopropyl alcohol and removed.
35 The product in which the unreacted materials had been removed was filtered and dried to obtain 4-[2-(4-diethylacetylphenyl)ethenyl]pyridine (m.p. 258-262°C, yield:

about 60%).

Example 2

2-Picoline (8.09 g) and terephthalaldehydamono(di-ethylacetal) (18.1 g) were added to a mixed solvent of acetic acid (6.81 g) and acetic anhydride (14.58 g), and the mixture was heated under reflux for 9 hours. Upon cooling the reaction mixture, a slurry was precipitated. The slurry was dispersed in an excess amount of water and the dispersion was neutralized to pH=7 by using 5 % by weight of potassium hydroxide aqueous solution. As the neutralization of the slurry processed, pale yellow precipitation was occurred. The product obtained by filtering the precipitation was dispersed in a cold (5°C) mixed solution of 5 % by weight of pure water and 95 % by weight of isopropyl alcohol, and the dispersion was stirred for 1 hour to remove the unreacted reactants and other solvents, filtered again, and dried to obtain 16 g of 2-[2-(4-diethylacetylphenyl)ethenyl]pyridine (m.p. 234-238°C).

Example 3

After dispersing 4-[2-(4-diethylacetylphenyl)ethenyl]-pyridine (10 g) prepared according to Example 1 in 180 ml of water, 4.45 g of dimethyl sulfate was added thereto and temperature of the mixture was raised to 40°C. As temperature was raised, the reactant was converted to SbQ-A salt and slurry phase of the reactant became a completely homogeneous phase. Water contained in the solution was removed by using rotary evaporator. The residue was washed with acetone, filtered and dried to obtain 12 g of 1-methyl-4-[2-(4-diethylacetylphenyl)ethenyl]pyridinium methosulfate (m.p. 163.88°C, λ_{max} = 343 nm). According to the same procedure as described above, 1-methyl-2-[2-(4-diethylacetylphenyl)ethenyl]pyridinium methosulfate by using 2-[2-(4-diethylacetylphenyl)ethenyl]pyridine and dimethyl sulfate.

Example 4

4-Picoline (22.35 g) was dissolved in methyl alcohol

(59.46 ml), and the solution was cooled in an ice-salt bath. Dimethyl sulfate (30.27 g) was added to the solution to proceed with a formation of a picolinium salt. After stirring for an hour, terephthalaldehydemono(diethylacetal) (50 g), and piperidine (2.3 g) as a catalyst were added thereto, and the mixture was heated under reflux for 9 hours. After the completion of the reaction, methyl alcohol solvent was removed by using a rotary evaporator, and the residue was sufficiently washed with acetone and dried to obtain 57 g of 1-methyl-4-[2-(4-diethylacetylphenyl)ethenyl]pyridinium methosulfate (m.p. 163.88°C, λ_{max} = 343 nm).

Example 5

4-Methylquinoline (25.72 g) was dissolved in methyl alcohol (32.53 ml), and the solution was cooled in an ice-salt bath. Methyl p-toluenesulfonate (29.84 g) was slowly added to the solution to proceed with formation of a quinolinium salt. After stirring for an hour, terephthalaldehydemono(diethylacetal) (42 g), and piperidine (1.27 g) as a catalyst were added thereto, and the mixture was heated under reflux for 15 hours. After the completion of the reaction, methyl alcohol solvent was removed, and the residue was sufficiently washed with acetone and dried to obtain 57 g of 1-methyl-4-[2-(4-dimethylacetylphenyl)ethenyl]quinolinium p-toluenesulfonate (m.p. 183°C, λ_{max} = 378 nm).

Example 6

2-Methylquinoline (12.63 g) was dissolved in methyl alcohol (16.26 ml), and the solution was cooled in an ice-salt bath. Bromobutane (21.54 g) was slowly added to the solution to proceed with formation of a quinolinium salt. After continuous stirring for 40 minutes, terephthalaldehydemono-(dibenzylacetal) (47 g), and piperidine (0.97 g) as a catalyst were added thereto, and the mixture was heated under reflux for 11 hours. After the completion of the reaction, methyl alcohol solvent was removed by using a rotary evaporator, and the residue was sufficiently washed with acetone and dried to

obtain 49 g of 1-butyl-2-[2-(4-dibenzylacetyl-phenyl)ethenyl]quinolinium bromide (m.p. 218-221°C, λ_{max} = 407 nm).

5 **Example 7**

4-Picoline (10.96 g) was dissolved in methyl alcohol (29.31 ml), and the solution was cooled in an ice-salt bath. Benzyl chloride (15.16 g) was slowly added to the solution to proceed with formation of a picolinium salt. After continuous
10 stirring for 50 minutes, terephthalaldehydemono(dimethylacetal) (28 g), and piperidine (1.35 g) as a catalyst were added thereto, and the mixture was heated under reflux for 13 hours. After the completion of the reaction, methyl alcohol solvent was removed by using a rotary evaporator, and the residue was
15 sufficiently washed with acetone and dried to obtain 26 g of 1-benzyl-4-[2-(4-dimethylacetylphenyl)ethenyl]pyridinium chloride (m.p. 110-115°C, λ_{max} = 348 nm).

Example 8

20 4-methylquinoline (21.75 g) was dissolved in methyl alcohol (31.17 ml), and the solution was cooled in an ice-salt bath. Dimethyl sulfate (21.35 g) was slowly added to the solution to proceed with formation of a methylquinolinium salt. After continuous stirring for 1 hour, terephthalaldehydemono-
25 (diethylacetal) (25 g), and piperidine (0.87 g) as a catalyst were added thereto, and the mixture was heated under reflux for 14 hours. After the completion of the reaction, methyl alcohol solvent was removed by using a rotary evaporator, and the residue was sufficiently washed with acetone and dried to
30 obtain 30 g of 1-methyl-4-[2-(4-diethylacetylphenyl)ethenyl]quinolinium methosulfate (m.p. 194-197°C, λ_{max} = 376 nm).

35 **Comparative Example 1**

γ -Picoline (9.40 g) was added to methanol (25 ml), and the solution was cooled in an ice-salt bath. After adding

dimethyl sulfate (12.61 g), the solution was stirred for 1 hour. Terephthalaldehyde (40.2 g, 3-fold excess amount of picoline), which is solid at room temperature, was added thereto and dissolved by heating. When the mixture became a homogeneous phase, 1.4 ml of piperidine was added, and the resultant mixture was heated under reflux for 5 hours. After 5 hours, dimeric by-products were deposited as yellow crystals, which was removed by hot filtration. The hot reaction mixture of which the dimeric by-products had been removed was added to a mixed solvent of ethanol (150 ml) and acetone (50 ml), and the resultant mixture was left overnight. Precipitated reaction product was filtered, sequentially washed with ethanol and acetone to obtain a yellow product of 1-methyl-4-[2-(4-formylphenyl)ethenyl]pyridinium methosulfate (yield: 52%, m.p. 210-213°C, λ_{max} =342 nm).

Comparative Example 2

N-Methyl- γ -picolinium p-toluenesulfonate (9.0 g) and TA (13.4 g) were dissolved in 20 ml of methanol, and 5 drops of piperidine were added thereto, and the resultant mixture was heated under reflux for 1 hour and a half. After cooling, ethyl acetate was added thereto, and the mixture was stood for 1 hour. Deposited crystals were filtered and washed with ethyl acetate to obtain 7.5 g of N-methyl- γ -(p-formylstyryl)pyridinium p-toluenesulfonate (m.p. 236-245°C, λ_{max} (H₂O)=343 nm).

Example 9

To a reactor containing 35.25 ml of methyl alcohol, 2-methyl quinoline (19.71 g) was added and dissolved. The temperature of the mixture was lowered to 0°C. To the solution, iodomethane (10.25 g) was slowly added to proceed with the formation of methyl quinolinium salt. After completely adding iodomethane, the mixture was stirred for 1 hour. Then terephthalaldehydemono(dimethylacetal) (26 g), and piperidine as a catalyst were added thereto, and the resultant mixture was heated under reflux for 13 hours. The reaction

mixture where the reaction had been ceased was cooled to room temperature, and methyl alcohol solvent was removed by using a vacuum evaporator. The residue was sufficiently washed with acetone and dried to obtain 29.8 g of 1-methyl-2-[2-(4-dimethylacetylphenyl)ethenyl]quinolinium iodide (m.p. 209-212°C, $\lambda_{\text{max}}=407$ nm).

Example 10

PVA (8 g) was added to water (112 ml), and dissolved by stirring at 40°C for 5 hours. The remaining PVA undissolved was removed by using a fine wire net. To the aqueous PVA solution, 1-methyl-4-[2-(4-diethylacetylphenyl)ethenyl]pyridinium methosulfate (SbQ-A salt) (0.72 g) prepared in Example 4 was added and dissolved, and then 85 % by weight of phosphoric acid (0.38 g) was added thereto. Stirring was continued for 40 hours in a darkroom while maintaining the temperature at 20°C to prepare a photosensitive resin. The photosensitive liquid wherein the reaction had been completed was re-precipitated in acetone and extracted with methanol solvent by using Soxhlet device for 8 hours. After extraction and drying, the product was dissolved in distilled water, and the light-absorbing range was examined. The product exhibited a maximum absorbance at 341 nm. The photosensitive liquid itself which had not been passed through the re-precipitation and extraction steps also showed high photosensitivity.

Example 11

4-[2-(4-Diethylacetylphenyl)ethenyl]pyridine (5 g) prepared in Example 1 was dispersed in 42 ml of water, and dimethylsulfate (2.23 g) was added thereto to prepare 1-methyl-4-[2-(4-diethylacetylphenyl)ethenyl]pyridinium methosulfate. At this time, the dispersion was converted to a homogeneous phase as the salt was produced. To the solution, 85 % by weight of phosphoric acid (3.74 g) was added, and the resultant solution was added to an aqueous PVA solution. The mixture was reacted in a darkroom for 44 hours, to obtain PVA-SbQ photosensitive liquid. The photosensitive liquid where the

reaction had been completed was treated with the same method as Example 10 and absorption range thereof was examined. It also showed a maximum absorbance at 341 nm. The photosensitive liquid itself which had not been passed through the treatment steps after reaction also showed high photosensitivity.

Example 12

PVA (20 g) was added to water (230 ml), and dissolved by stirring at room temperature for 4 hours. The remaining PVA undissolved was removed by using a fine wire net. To the aqueous PVA solution, 1-methyl-2-[2-(4-diethylacetylphenyl)ethenyl]quinolinium iodide (2.13 g) prepared in Example 9 was added and dissolved, and then 80 % by weight of phosphoric acid (1.03 g) was added thereto. Stirring was continued for 35 hours in a darkroom while maintaining the room temperature to prepare a photosensitive resin. The photosensitive liquid where the reaction had been completed was re-precipitated in acetone and extracted with methanol solvent by using Soxhlet device for 8 hours. After extraction and drying, the product was dissolved in distilled water, and the light-absorbing range was examined. The product exhibited a maximum absorbance at 341 nm. The photosensitive liquid itself which had not been passed through the re-precipitation and extraction steps also showed high photosensitivity.

Comparative Example 3

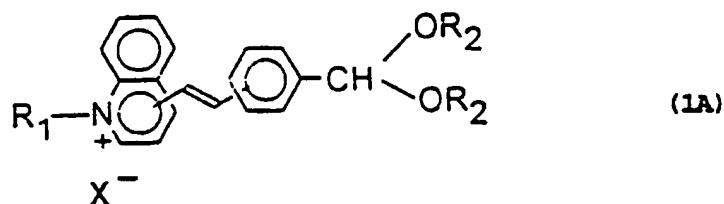
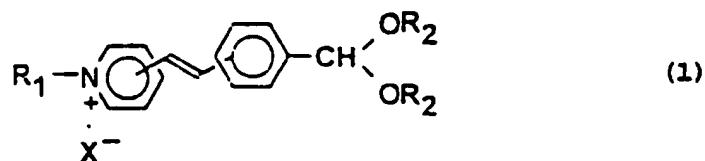
After dissolving PVA (50 g) in pure water (600 ml), 1-methyl-4-[2-(4-formylphenyl)ethenyl]pyridinium methosulfate (4.52 g) was added and dissolved therein. To the solution, 80 % aqueous solution of phosphoric acid (8 g) was added, and the mixture was stirred at room temperature for 24 hours. The reaction-completed mixture was added to acetone to form a precipitation, and extracted with methanol by using Soxhlet device to remove the unreacted SbQ salt. The PVA-SbQ was dissolved in pure water again, and the absorbance was examined. It exhibited a maximum absorbance at 340 nm.

Comparative Example 4

Polyvinyl acetate (PVA) (500 mg) having polymerization degree of 1700 and saponification ratio of 87 % was dissolved in distilled water (7 ml), and 1-methyl-4-[p-(2,2-dimethoxyethoxy)styryl]pyridinium p-toluenesulfonate (55 mg) was dissolved therein. To the solution, 85 % by weight of phosphoric acid (500 mg) was added, and the mixture was stirred at 60°C for 15 hours. The resultant yellow reaction mixture was added to a large amount of acetone to precipitate resin. The resin was sufficiently washed twice with methanol, and dried in vacuo to obtain 420 mg of the product. The resin exhibited a maximum absorption peak at 370 nm in an aqueous solution, and the incorporation ratio of stilbazolium group was 0.71 mol%. The resin film showed 9-fold increase of sensitivity as compared to cinnamon vinyl.

WHAT IS CLAIMED IS:

1. Stilbazolium salt represented by following formula (1) or (1A):



wherein, R_1 and R_2 , being identical to or different from each other, independently represents hydrogen atom, alkyl group, aryl group, allyl group, aralkyl group or allylalkyl group, wherein hydroxyl group, amide group, carboxylic group, ether bond, double bond, or the like may be included in each group; and X^- represents halogen ion, sulfate ion, phosphate ion, methosulfate ion, methanesulfonate ion or p-toluenesulfonate ion.

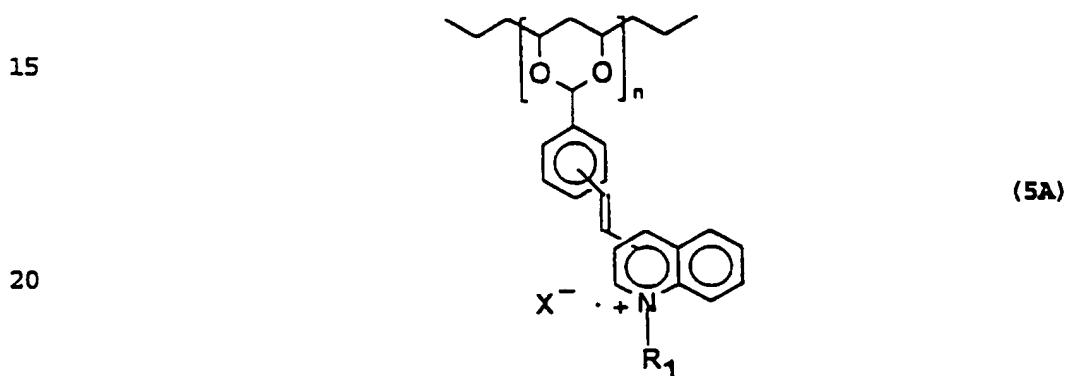
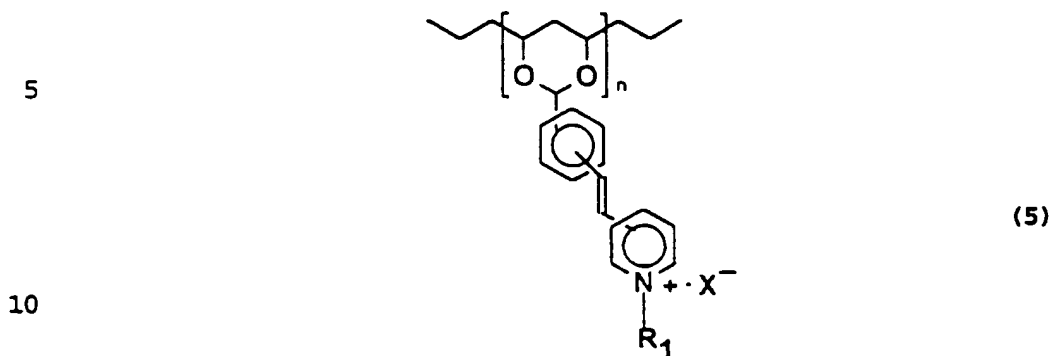
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2. Use of the stilbazolium salt according to claim 1 as a photoreactive compound, by incorporating it to PVA, for preparing a photosensitive resin of following formula (5) or (5A) which cause a cross-linking reaction by light.

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25 In the formulas, R_1 and X^- are as defined in claim 1.

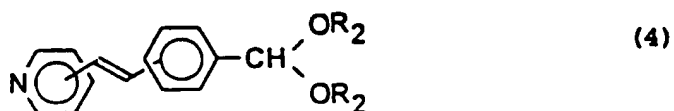
3. A process for preparation of the stilbazolium salt in accordance with claim 1, which comprises:

30 reacting a compound of picolines or methylquinolines with TDA of following formula (2);

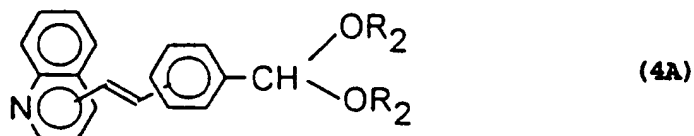
purifying the reaction product to obtain an intermediate represented by following formula (4) or (4A); and

35 dispersing the intermediate thus obtained in water and adding an alkylating agent of following formula (3) thereto to obtain the stilbazolium salt;

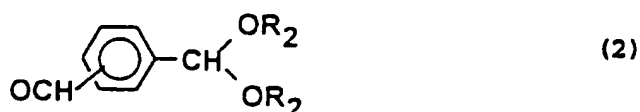
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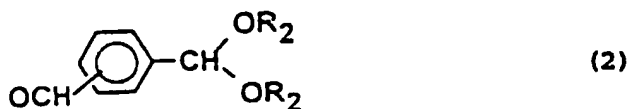
wherein, R_1 and R_2 are defined as claim 1; and X represents halogen atom, sulfate group, phosphate group, methosulfate group, methanesulfonate group or p-toluenesulfonate group.

4. A process for preparation of the stilbazolium salt in accordance with claim 1, which comprises:

reacting a compound of picolines or methylquinolines with an alkylating agent of following formula (3) to form a picolinium salt or methylquinolinium salt; and

adding TDA of following formula (2) to the solution thus obtained and heating under reflux to obtain a stilbazolium salt;

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 $R_1 - X$

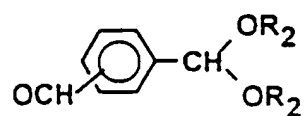
(3)

wherein, R_1 , R_2 and X are defined as claim 3.

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5. Use of the compound represented by following formula
(2) for preparing a stilbazolium salt in accordance with claim
1;

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(2)

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wherein, R_2 is as defined in claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 96/00035

A. CLASSIFICATION OF SUBJECT MATTER IPC ⁶ : C 07 D 213/46, 215/14; G 08 F 8/30, 8/32; G 03 C 1/71 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC ⁶ : G 08 F 8/00; C 07 D 215/00, 213/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AT, Chem. Abstr. Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Questel DARC, WPIL, CAS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages.	Relevant to claim No.
X	Chemical Abstracts, Vol.107, No.14, 05 October 1987 (Columbus, Ohio, USA), page 24, column 1, abstract No.116314n, ICHIMURA, K. et al.: "Photocrosslinkability of photosensitive poly(vinyl alcohol) having styryl-quinolinium groups", & Sen'i Kobunshi Zairyo Kenkyusho 1987, (155), 37-44 (Japan). CN: 110241-43-5 (4[2-[4-(dimethoxymethyl)phenyl]=ethenyl]-1-methyl-quinolinium-methylsulfat.....	1
X,P	Chemical Abstracts, Vol.124, No.8, 19 February 1996 (Columbus, Ohio, USA), page 19, column 2, abstract No.88080p, PARK, Lee-Soon et al.: "Synthesis and photochemical properties of water soluble photosensitive polymer based on poly(vinyl alcohol)", & Pollimo 1995, 19(5), 715-21 (Korea).	1-5
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C... <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 15 May 1996 (15.05.96)		Date of mailing of the international search report 07 June 1996 (07.06.96)
Name and mailing address of the ISA/ AT AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/535		Authorized officer Hammer Telephone No. 1/5337058/44

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR 96/00035

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	DE 31 14 468 A1 (SONY CORP.) 04 March 1982 (04.03.82), claims 1-3.	2
A	Patent Abstracts of Japan, Vol.14, No.65 (E-884), 1990, JP 63-113525 (SONY CORP.).	2
A	Patent Abstracts of Japan, Vol.13, No.553 (C-663), 1989, JP 63-54938 (AGENCY OF IND. SCIENCE & TECHNOL.).	2
A	Patent Abstracts of Japan, Vol.9, No.6 (P-326), 1985, JP 58-27073 (OUJI SEISHI K.K.).	2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 96/00035

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		FR A1 2483638	04-12-81
		FR B1 2483638	18-12-87
		GB A1 2076826	09-12-81
		GB B2 2076826	04-04-84
		JP A2 56147804	17-11-81
		NL A 8101912	16-11-81
		US A 4339524	13-07-82